

**DOSIMETRIC PROPERTIES OF GERMANIUM DOPED CALCIUM
BORATE GLASS FOR USE AS PHOTON DOSIMETER**

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DOSIMETRIC PROPERTIES OF GERMANIUM DOPED CALCIUM BORATE
GLASS FOR USE AS PHOTON DOSIMETER

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A thesis submitted in fulfillment of the
requirements for the award of the degree of
Master of Science (Physics)

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Teknologi Malaysia

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I specially dedicate this work

To my dear parents Tengku Kamarul Bahri bin
Tengku Kamarul Zaman Azizan binti Mohd Ismail

To my family's member
Whose love, kindness, patience and prayer have brought me this far

To my supervisors, friends And Everybody
that have contributed For their love,
understanding and support

Thank you very much!!!

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In the name of Allah, the Most Gracious, Most Merciful. Praise be to Allah S.W.T, Peace and blessings of Allah be upon His Messenger, Muhammad S.A.W. and all his family and companions.

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Jazakum Allahu khairan, and peace to all.

ABSTRACT

Borate glasses have been widely studied due to their features as glass formers and present a very useful material for radiation dosimetry applications. The fundamental properties of germanium doped calcium borate glass; $(30-x)\text{CaO} \cdot 70\text{B}_2\text{O}_3 \cdot x\text{GeO}_2$ ($x = 0.1, 0.2, 0.3, 0.4$ and 0.5 mol%) prepared using melt-quenching method were investigated. The physical properties including the amorphous state, density and molar volume were measured. The structural analyses were carried out using infrared transmission spectra and optical properties were determined from ultraviolet-visible optical spectra. Weight fraction obtained from energy dispersive X-ray spectrometry analysis leads to the determination of the effective atomic number of the sample. The total mass attenuation coefficients at photon energies of 0.662 MeV and 1.25 MeV were also calculated by using WinXCom software. Thermoluminescence properties measurements were performed by irradiating the glasses with ^{60}Co gamma ray, 6 MV and 10 MV photon beam with doses ranging from 0.5 Gy to 4.0 Gy. The amorphous phases of the glass samples were identified from this study. The effective atomic number of glass sample was found to be between 11.70 to 12.52 for GeO_2 concentration of 0.1 to 0.5 mol%. The values are quite close to the effective atomic number of the bone, which is 14. The densities, absorption band, molar volumes, optical band gap and refractive index indicate that GeO_2 acts differently on the glass structure over their compositions. The glow curves were analysed to determine various thermoluminescence characteristics of the glass samples. The glass sample with GeO_2 concentration of 0.1 mol% has the best thermoluminescence characteristics such as linearity, sensitivity, fading and reproducibility. In conclusion, germanium doped calcium borate glass has potential to be considered as thermoluminescence dosimeter.

ABSTRAK

Kaca borat telah dikaji dengan meluas berikutan cirinya sebagai kaca pembentuk dan menunjukkan bahan yang sangat berguna untuk penggunaan dosimetri sinaran. Ciri asas kaca kalsium borat terdop dengan germanium; $(30-x)\text{CaO} - 70\text{B}_2\text{O}_3 : x\text{GeO}_2$ ($x = 0.1, 0.2, 0.3, 0.4$ dan 0.5 mol%) yang telah disediakan menggunakan teknik pelindapan lebur telah dikaji. Ciri fizikal termasuklah fasa amorfus, ketumpatan dan isipadu molar telah diukur. Analisis struktur dikaji menggunakan spektrum penghantaran inframerah dan ciri optik telah ditentukan daripada spektrum optik ultraungu-nampak. Pecahan berat yang diperoleh daripada analisis spektrometer sebaran tenaga sinar-X membolehkan penentuan nombor atom berkesan sampel kaca. Pekali pengecilan jisim keseluruhan pada tenaga foton 0.662 MeV dan 1.25 MeV juga dihitung menggunakan perisian WinXCom. Pengukuran ciri termopendarcahaya dilakukan dengan menyinarakan sampel kaca dengan sinar gama ^{60}Co , alur foton 6MV dan 10MV pada julat dos antara 0.5 Gy hingga 4.0 Gy. Fasa amorfus bagi semua sampel kaca telah dikenalpasti dalam hasil kajian ini. Nombor atom berkesan sampel kaca yang ditentukan bernilai antara 11.70 hingga

12.52 bagi kepekatan GeO_2 antara 0.1 hingga 0.5 mol%. Nilai ini hampir sama dengan nombor atom berkesan bagi tulang, iaitu 14 . Ketumpatan, jalur serapan, isipadu molar, jurang jalur optik dan indeks biasan menunjukkan GeO_2 berfungsi secara berbeza ke atas struktur kaca mengikut komposisi. Lengkung berbara yang diperoleh dianalisis bagi menentukan pelbagai ciri sampel kaca tersebut. Sampel kaca yang mempunyai kepekatan GeO_2 0.1 mol% didapati mempunyai ciri termopendarcahaya seperti kelinearan, kepekaan, kelunturan dan kebolehgunaan semula yang terbaik. Sebagai kesimpulan, kaca kalsium borat terdop dengan germanium mempunyai keupayaan untuk dipertimbangkan sebagai dosmeter termopendarcahaya.

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LIST OF SYMBOLS

Mean thermoluminescence background signal
Standard deviation

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CHAPTER 1

INTRODUCTION

1.1 Research background

Thermoluminescence dosimetry is used in many scientific and applied fields such as radiotherapy, radiation protection, industry, clinic, and space and environment research, using many different materials. In general, the basic demands of a thermoluminescence material to be used for dosimetric are low hygroscopicity, large linearity, energy non dependence and high sensitivity for a low dose measurements. After Daniels et al. (1953) first applied the thermoluminescence (TL) phenomenon on dosimetry use, research on thermoluminescence continued in the twenty-first century. Borate compounds are among inorganic materials that have been studied with respect to the TL dosimetry requirements. Borates are extensively studied because of its easy preparation, low cost and high sensitivity compared to other TL materials (Jiang et al., 2009). Since these borate compounds show an effective atomic number close to that of human tissue ($Z_{eff} = 7.42$), borates become the best choice materials to be used in medical and environmental dosimetry (Rojas et al., 2006). So far, research on thermoluminescence characteristics of borate compounds focuses on lithium borate. Lithium borate compounds are considered due to their low cost, near tissue equivalent absorption coefficient ($Z_{eff} = 7.3$) and easy handling process. Schulman et al. (1965) are the first to be acknowledged for starting the TL studies on lithium borate compounds and then, various TL studies of alkali and alkaline earth tetra borates are continued up to present times especially on magnesium and lithium borate compounds.

1.2 Statement of the problem

A glass system composed from B_2O_3 , modified by oxide of CaO and doped with GeO_2 is studied. Germanium makes the sample become glass because it can form a highly cross-linked network of chemical bonds. Calcium oxide is used as the modifier in order to have highly stable and durable phosphor. So far, the studies of thermoluminescence characteristics are concerned on magnesium and lithium borate glass. There is very few work done on the combination of borate, calcium oxide and germanium. Therefore, in this work thermoluminescence properties of germanium doped calcium borate glass subjected to photon irradiation are investigated.

1.3 Objectives of study

The aim of this study is to investigate the fundamental properties of germanium doped calcium borate glass which can be use for thermoluminescence dosimeter. The overall objectives are summarized as follows:

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1.4 Scope of study

In order to achieve the objectives, the following scopes are carried out:

i) Preparations of germanium doped calcium borate glasses using melt quenching technique. ii) Determination vitreosity of germanium doped calcium borate glasses using X-ray diffraction technique. iii) Determination concentration of germanium doped calcium borate glasses using energy dispersive X-ray analysis. iv) Determination density and molar volume of germanium doped calcium borate glasses. v) Determination optical study of germanium doped calcium borate glasses using ultraviolet-visible (UV-Vis) optical spectra. vi) Determination structural information of germanium doped calcium borate glasses using fourier transform infrared (FTIR) transmission spectra.

vii) Determination total mass attenuation coefficients and partial interactions of germanium doped calcium borate glasses at photon energies of 0.662 MeV and 1.25 MeV by using WinXCom software.

viii) Perform glass samples irradiation using gamma radiation using ^{60}Co . ix) Perform glass samples irradiation to 6 MV and 10 MV photon using PRIMUS MLC 3339 linear accelerator (LINAC). x) Determination of TL properties using TLD reader model 4500 Harshaw.

1.5 Significance of study

This study may provide a basis for exploiting TL phenomena of calcium borate doped with germanium. General characteristics consist of linearity, sensitivity, re-use, reproducibility, effective atomic number and fading may provide germanium doped calcium borate glasses to be introduced as a new thermoluminescence dosimeter particularly in environmental dosimeter and radiation therapy application. It is hoped that results from this study will help the development of this new material

and will establish germanium doped calcium borate glass a very potential and recommended glassy detector that can be used in many applications.

1.6 Report outline

Chapter 1 is a brief introduction of the study that consists of problem statements, objectives of the study, scope, significance, and finally thesis outline. Literature review is in Chapter 2, which covers glass and thermoluminescence theory, advantages of borate, calcium and germanium. Chapter 3 explains the experimental methods used starting from the glass preparation, physical, structural and optical methods of X-ray diffraction (XRD), density and molar volume measurements, fourier transform infrared (FTIR) spectroscopy as well as ultraviolet-visible (UV-Vis) spectroscopy. Determination of effective atomic number from energy dispersive X-ray (EDX) analysis results and mass attenuation coefficients using WinXCom software also include in this chapter. These measurements are ending up with TL glow curves analysis. Chapter 4 presents and discusses results obtained from germanium doped calcium borate glass systems. Last but not least, Chapter 5 provides the summarization results from this study and gives some recommendations for future study.

REFERENCES

- American National Standards Institute. *Performance, Testing, and Procedural Specification for Thermoluminescence Dosimetry (Environmental Applications)*. New York, ANSI N545. 1975.
- Balogun, F.A., Ogundare, F.O. and Fasasi, M.K. (2003). TL response of sodalime glass at high doses. *Nuclear Instruments and Methods in Physics Research Section A*. 505 (1-2), 407-410.
- C162 (1945). *Compilation of ASTM Standard Definitions*. The American Society for Testing Materials, Philadelphia PA.
- Chen, R. and McKeever, S. W. S. (1997). *Theory of Thermoluminescence and Related Phenomena*. Singapore: World Scientific.
- Chialanza, M.R, Castiglioni, J. and Fornaro, L. (2012). Crystallization as a way for inducing thermoluminescence in a lead borate glass. *Journal of Materials Science*. 47 (5), 2339-2344.
- Correcher, V., García-Guinea, J. and Rivera, T. (2009). Thermoluminescence sensitivity of daily use materials. *Radiation Effects and Defects in Solids*. 164(4), 232-239.
- Dhoble, S. J., Gedam, S. C., Nagpure, I. M. and Moharil, S. V. (2008). Luminescence of Cu⁺ in halosulphate phosphor. *Journal of Materials Science*. 43, 3189–3192.
- Daniels, F., Boyd, C.A. and Saunders, D.F. (1953). Thermoluminescence as a research tool. *Science*. 117, 343-349.
- Davis, S. D., Ross, C. K., Mobit, P. N., Van der Zwan, L., Chase, W. J. and Shortt, K. R. (2003). The response of LiF thermoluminescence dosimeters to photon beams in the energy range from 30 kV xrays to 60Co gamma rays. *Radiation Protection Dosimetry*. 106, 33–43.
- Depci, T., Ozbayoglu, G., Yilmaz, A. and Yazici, A. N. (2008). The thermoluminescent properties of lithium triborate (LiB₃O₅) activated by

aluminium. *Nuclear Instrument and Methods in Physics Research B.* 266, 755-762.

Dimitrov, V. and Komatsu, T. (2002). Classification of simple oxide: a polarizability approach. *Journal of Solid State Chemistry.* 163, 100-112.

Elkholy, M. M. (2010). Thermoluminescence of B₂O₃ – Li₂O glass system doped with MgO. *Journal of Luminescence.* 130, 1880-1892.

Engin, B., Ayda, C. and Demirta, H. (2010). Study of the thermoluminescence dosimetric properties of window glass. *Radiation Effects and Defects in Solids.* 165, 54-64.

Eraiah, B., and Bhat, Sudha G. (2007). Optical properties of samarium doped zinc-phosphate glasses. *Journal of Physics and Chemistry Solids.* 68, 581-585.

Ferreira, C. C., Ximenes, R. E., Garcia, C. A. B., Vieira, J. W. and Maia, A. F. (2010). Total mass attenuation coefficient evaluation of ten materials commonly used to simulate human tissue. *Journal of Physics: Conference Series* 249, 012029.

Furetta, C. (2003). *Handbook of Thermoluminescence.* Singapore: World Scientific.

Furetta, C., Prokic, M., Salamon, R. and Kitis, G. (2000). Dosimetric characterization of a new production of MgB₄O₇: Dy, Na thermoluminescent material. *Applied Radiation and Isotopes.* 52, 243-250.

Furetta, C., Prokic, M., Salamon, R., Prokic, V. and Kitis, G. (2001). Dosimetric characteristics of tissue equivalent thermoluminescent solid TL detectors based on lithium borate. *Nuclear Instruments and Methods in Physics Research Section A.* 456 (3), 411-417.

Gerardy, I. (2009, April 21). The thermoluminescence dating face to produce a new type of false. *CeROArt*. Retrieved January 7, 2014, from <http://ceroart.revues.org/1089>.

Gerward, L., Guilbert, N., Jensen, K. B. and Levring, H. (2001) X-ray absorption in matter: Reengineering XCOM. *Radiation Physics and Chemistry.* 60, 23-24.

Glennie Gilbert Douglas (2003). *A Comparison of TLD: LiF:Mg,Ti and LiF:Mg,Cu,P, for Measurement of Radiation Therapy Doses.* Doctor of Philosophy. University of Virginia.

González, P.R., Furetta, C., Calvo, B.E., Gaso, M.I. and Cruz-Zaragoza, E. (2007). Dosimetric characterization of a new preparation of BaSO₄ activated by Eu ions. *Nuclear Instruments and Methods in Physics Research B.* 260, 685-692.

Gowda, S., Krishnaveni, S., Yashoda, T., Umesh, T.K. and Gowda, R. (2004). Photon mass attenuation coefficients, effective atomic numbers and electron densities of some thermoluminescent dosimetric compounds. *PRAMANA-Journal of Physics*. 63, 529-541.

Gurler, O., Oz, H., Yalcin, S. and Gundogdu, O. (2009). Mass absorption and mass energy transfer coefficients for 0.4-10 MeV gamma rays in elemental solids and gases. *Applied Radiation and Isotopes*. 67 (1), 201-205.

Hasegawa, B. (1987). *Physics of Medical X-Ray Imaging*. (2nd ed.) Madison, Medical Physics Publishing Corporation.

Hashim, S., Al-Ahbabi, S., Bradley, D.A., Webb, M., Jeynes, C., Ramli, A.T. and Wagirann H. (2009). The thermoluminescence response of doped SiO₂ optical fibres subjected to photon and electron irradiations. *Applied Radiation and Isotopes*. 67, 423-427.

Hashim, S., Bradley, D.A., Peng, N., Ramli, A.T. and Wagiran, H. (2010a). The thermoluminescence response of oxygen-doped optical fibres subjected to photon and electron irradiations. *Nuclear Instruments and Methods in Physics*

A. 619 (1-3), 291-294.

Hashim, S., Bradley, D.A., Saripan, M.I., Ramli, A.T. and Wagiran, H. (2010b). The thermoluminescence response of doped SiO₂ optical fibres subjected to fast neutrons. *Applied Radiation and Isotopes*. 68 (4), 700-703.

Hossain, I., Wagiran, H., Asni, H. (2012). Mass energy absorption coefficient for 0.2-20 MeV photon in Ge-doped optical fiber and TLD-100 by Monte Carlo n-particle code version 5 (MCNP5). *Optoelectronics and Advanced Materials, Rapid Communications*. 9 (1-2), 162-164.

Hubbell, J. H. (1982). Photon mass attenuation and energy-absorption coefficients from 1 keV to 20 MeV. *The International Journal of Applied Radiation and Isotopes*. 33, 1269-1290.

Hubbell, J. H. and Seltzer, S. M. (1996). *Tables of X-Ray Mass Attenuation Coefficients and Mass Energy Absorption Coefficients from 1 keV to 20 MeV for Elements Z=1 to 92 and 48 Additional Substances of Dosimetric Interest*. Gaithersburg, Maryland: National Institute for Science and Technology; NIST 5632.

Hunda, B. M., Holovey, V. M., Turok, I. I. and Solomon, A. M. (2005). Effect of Melt Composition on the Luminescent Properties of Czochralski-Grown $\text{Li}_2\text{B}_4\text{O}_7$ Single Crystals. *Inorganic Materials*. 41, 1125-1129.

Hussin, R. (2011). *Structural studies of glass by Nuclear Magnetic Resonance*. Skudai, Johor: Penerbit Universiti Teknologi Malaysia Press.

ICRU Report 44 -International Commission on Radiation Units and Measurements. (1989). *Tissue Substitutes in Radiation Dosimetry and Measurements*. Bethesda, Maryland: ICRU Publications.

Jackson, D.F., and Hawkes, D.J. (1981). X-ray attenuation coefficients of elements and mixtures. *Physics Reports*. 70 (3), 169-233.

Jiang, L.H., Zhang, Y.L., Li, C.Y., Hao, J.Q. and Su, Q. (2009). Synthesis, photoluminescence, thermoluminescence and dosimetry properties of novel phosphor $\text{KSr}_4(\text{BO}_3)_3:\text{Ce}$. *Journal of Alloys and Compounds*. 482, 313-316.

John, V. (1992). *Introduction to Engineering Materials*. London: Macmillan.

Kamitsos, E.I., Karakessides, M.A. and Chryssikos, G.D. (1987). Vibrational spectra of magnesium-sodium-borate glasses: 2. Raman and mid-infrared investigation of the network structure. *The Journal Physical Chemistry*. 91, 1073-1079.

Kayhan, M. (2009). *Effect of synthesis and doping methods on thermoluminescence glow curves of manganese doped lithium tetraborate*. Master of Science, Middle East Technical University, Turkey.

Kim, J.L., Lee, J.I., Pradhan, A.S., Kim, B.H. and Kim, J.S. (2008). Further studies on the dosimetric characteristics of LiF:Mg,Cu,Si -A high sensitivity thermoluminescence dosimeter (TLD). *Radiation Measurement*. 43 (2-6), 446-449.

Kortov, V. (2007). Materials for thermoluminescent dosimetry: Current status and future trends. *Radiation Measurement*. 42 (4-5), 576-581.

Li, J., Hao, J. Q., Li, C. Y., Zhang, C. X., Tang, Q., Zhang, Y. L., Su, Q. and Wang, S. B. (2005). Thermally stimulated luminescence studies for dysprosium doped strontium tetraborate. *Radiation Measurement*. 39 (2), 229-233.

Li, J., Zhang, C. X, Tang, Q., Zhang, Y. L., Hao, J. Q., Su, Q. and Wang, S. B. (2007). Synthesis, photoluminescence, thermoluminescence and dosimetry properties of novel phosphor $\text{Zn}(\text{BO}_2)_2:\text{Tb}$. *Journal of Physics and Chemistry of Solids*. 68 (2), 143-147.

Limkitjaroenporn, P., Kaewkhao, J., Limsuwan, P. and Chewpraditkul, W. (2011). Physical, optical, structural and gamma-ray shielding properties of lead sodium borate glasses. *Journal of Physics and Chemistry of Solids*. 72, 245

251.

Lower, Nathan P., McRae, Justin L., Feller, Heidi A., Betzen, Ashlea R., Shalini Kapoor, Mario Affatigato and Feller, Steven A. (2001). Physical properties of alkaline-earth and alkali borate glasses prepared over an extended range of compositions. *Journal of Non-Crystalline Solids*. 293-295, 669-675.

Luo, Ling Z. (2008). Extensive fade study of Harshaw LiF TLD materials. *Radiation Measurements*. 43 (2-6), 365 – 370.

Mann, N., Kaur, U., Singh, T., Sharma, J.K. and Singh, P.S. (2010). Photon Interaction Parameters for Some Borate Glasses. *AIP Conference Proceedings*, 1324 (1), 407-410.

McKeever, S.W. and Chen, R. (1997). *Theory of Thermoluminescence and Related Phenomena*. Singapore: World Scientific publishing Co Pte Ltd.

McKeever, S.W.S. (1985) *Thermoluminescence of Solids*. Cambridge, England: Cambridge University Press.

McKeever, S.W.S., Moscovitch, M. and Townsend, P.D. (1995). *Thermoluminescence Dosimetry Materials: Properties and Uses*. Ashford, Kent, England: Nuclear Technology Publishing.

Mckinlay, A.F. (1981). *Thermoluminescence Dosimetry – Medical Physics Handbook 5*. Bristol: Adam Hilger Ltd.

Meijerink, A., Blasse, G. and Glasbeek, M. (1990). Photoluminescence, thermoluminescence and EPR studies on Zn₄B₆O₁₃. *Journal of Physics: Condensed Matter*. 2 (29), 6303-6313.

Model4500 Manual TLD Reader with WinREMS: Operator's Manual (2005). 4500-W-O-0805-005. Madison: Thermo Electron Corporation.

Narayan, P., Vaijapurkar, S. G., Senwar, K. R., Kumar, D. and Bhatnagar, P. K. (2008). Accidental gamma dose measurement using commercial glasses. *Radiation Protection Dosimetry*. 130 (3), 319–324.

Natarajan, V. (2009). Application of spectroscopic techniques in the radiation dosimetry of glasses: An update. *International Seminar on Science and Technology of Glass Materials (ISSTGM-2009) IOP Publishing IOP Conf. Series: Materials Science and Engineering*. 2, 012010.

- Pablo, G. D. and Frank, H. S. (2001). Supercooled liquids and the glass transition. *Nature*. 410, 259-267.
- Park, K. S., Ahna, J. K., Kima, D. J., Kima, H. K. and Wanga, H. Y. H. (2002). Growth and properties of $\text{Li}_2\text{B}_4\text{O}_7$ single crystals. *Journal of Crystal Growth*. 249, 483-486.
- Patil, R. R. and Moharil, S. V. (2003). Thermoluminescence in some copper-doped compounds. *Physica Status Solidi (a)*. 199, 527-529.
- Pekpak, E., Yilmaz, A. and Ozbayoglu, G. (2010). An Overview on Preparation and TL Characterization of Lithium Borates for Dosimetric Use. *The Open Mineral Processing Journal*. 3, 14-24.
- Pisarski, W.A., Joanna Pisarska, J. and Romanowski, W. R. (2005). Structural role of rare earth ions in lead borate glasses evidenced by infrared spectroscopy: $\text{BO}_3 \leftrightarrow \text{BO}_4$ conversion. *Journal of Molecular Structure*. 744-747, 515-520.
- Pradhan, A. S. (1981). Thermoluminescence Dosimetry and its Applications. *Radiation Protection Dosimetry*. 1 (3), 153-167.
- Priharti, W., Samat, S.B. and Kadir, A.B.A. (2013). Uncertainty analysis of Hp (10) meas/ Hp (10) del ratio for TLD-100H at energy 24-1250 keV. *Jurnal Teknologi*. 62, 115-118.
- Prokic, M. (2002). Dosimetric characteristics of $\text{Li}_2\text{B}_4\text{O}_7$: Cu, Ag, P solid TL detectors. *Radiation Protection Dosimetry*. 33, 265-268.
- Rabie, N., Abbas, A.F. and Ali, A.A. (1999). Thermoluminescence properties of cabal glasses doped with some rare-earth metal oxides. *Indian Journal of Pure and Applied Physics*. 37, 914-920.
- Rachkovskaya, G.E. and Zakharevich, G.B. (2002). Vitrification properties, and structure of lead-tellurite borate glasses. *Glass and Ceramics*. 59, 123-126.
- Rada, S., Pascuta, P., Culea, M., Maties, V., Rada, M., Barlea, M. and Culea, E. (2009). The local structure of europium-lead-borate glass ceramics. *Journal of Molecular Structure*. 924, 89-92.
- Raghavaiah, B.V., Rao, P.N., Reddy, P.Y. and Veeraiah, N. (2007). Thermoluminescence studies on $\text{PbO-Sb}_2\text{O}_3-\text{As}_2\text{O}_3$ glasses doped with iron ions. *Optical Materials*. 29 (5), 566.
- Rahim Sahar, Md. (2000). *Fizik Bahan Amorfus*. Skudai, Johor: Penerbit Universiti Teknologi Malaysia Press, 34-36.

Ramli, A.T., Bradley, D.A., Hashim, S. and Wagiran, H. (2009). The thermoluminescence response of doped SiO₂ optical fibres subjected to alpha-particle irradiation. *Applied Radiation Isotopes*. 67 (3), 428-432.

Rojas, S.S., Yukimitu, K. and Hernandez, A.C. (2008). Dosimetric properties of UV irradiated calcium co-doped borate glass-ceramic. *Nuclear Instruments and Methods in Physics Research B*. 266, 653-657.

Rojas, S.S., Yukimitu, K., de Camargo, A.S.S., Nunes, L.A.O. and Hernandez, A.C. (2006). Undoped and calcium doped borate glass system for thermoluminescent dosimeter. *Journal of Non-Crystalline Solids*. 352, 36083612.

Saddeek, Y.B. (2009). Structural and acoustical studies of lead sodium borate glasses. *Journal of Alloy and Compounds*. 467, 14-21

Santiago, M., Grasseli, C., Caselli, E., Lester, M., Lava, A. and Spano, F. (2001). Thermoluminescence of SrB₄O₇:Dy. *Physica Status Solidi (A)*. 185 (2), 285
289.

Santos, C.N., Yukimitu, K., Zanata, A.R. and Hernandez, A.C. (2006). Thermoluminescence of aluminophosphate glasses in the metaphosphate composition. *Nuclear Instruments and Methods in Physics Research Section A*. 246 (2), 374-378.

Schulman, J.H., Kirk, R.D. and West, E.J. (1965). Use of lithium borate for thermoluminescence dosimetry. *Proceedings International Conference on Luminescence Dosimetry, Conf: 650637*. 25, 113-117.

Shelby. (1997). Cer103 Notes Chapter 5 5-15. *R.K. Brow Glass Structure (2)*, 5-15.

Sidek H.A.A., Rosmawati S., Talib Z.A., Halimah M.K., and Daud W.M., (2009). Synthesis and Optical Properties of ZnO-TeO₂ Glass System. *American Journal of Applied Sciences*. 6 (8), 1489-1494.

Soliman, C. (2009). DyF₃: A promising new TL material for gamma dosimetry. *Nuclear Instruments and Methods in Physics Research B*. 267 (14), 24232426.

Spiers, F.W. (1946). Effective atomic number and energy absorption in tissues. *The British Journal of Radiology*. 19 (218), 52-63.

Takenaga, M., Yamamoto, O. and Yamashita, T. (1980). Preparation and characteristics of Li₂B₄O₇: Cu phosphor. *Nuclear Instruments and Methods*. 175, 77-78.

- U.S. Geological Survey (2008). Germanium—Statistics and Information. *U.S. Geological Survey, Mineral Commodity Summaries*. Retrieved on August 8, 2008, from <http://minerals.usgs.gov/minerals/pubs/commodity/germanium/>
- Varsamis, C.P., Kamitsos, E.I. and Chryssikos, G.D. (2000). Spectroscopic investigation of AgI-doped borate glasses. *Solid State Ionics*. 136, 1031-1039.
- Venkat Reddy, P., Laxmi Kanth, C., Prashanth Kumar, V., Veeraiah, N. and Kistaiah, P. (2005). Optical and thermoluminescence properties of R₂O–RF– B₂O₃ glass systems doped with MnO. *Journal of Non-Crystalline Solids*. 351 (49-51), 3752–3759.
- Wagiran, H., Hossain, I., Asni, H. and Ramli, A.T. (2012). Comparison of thermoluminescence energy response of optical fiber subject to photon irradiation between Monte Carlo simulation and experiments. *Journal of Engineering Thermophysics*. 21 (1), 90-94.
- Yaakob, N.H., Wagiran, H., Hossain, I., Ramli, A.T., Bradley, D.A., Hashim, S. and Ali, H. (2011). Electron irradiation response on Ge and Al-doped SiO₂ optical fibres. *Nuclear Instruments and Methods in Physics Research A*. 637, 186
189.
- Yiannopoulos, Y.D., Chryssikos, G.D. and Kamitsos, G.D. (2001). Structure and properties of alkaline earth borate glasses. *Physics and Chemistry of Glasses*. 42 (3), 164-172.
- Yoshimura, E.M., Okuno, E., Krajczyk, L. and Suszynska, M. (1998). Formation of silver colloids on ion exchanged soda lime silicate glasses by irradiation. *Nuclear Instruments and Methods in Physics Research B*. 141 (1-4), 304-307.
- Zeng, Q. H., Pei, Z. W., Su, Q. and Lu, S. Z. (1999a). Luminescence properties of S_{min} barium octaborates (BaB₈O₁₃ : Sm). *Journal of Luminescence*. 82 (3), 241-249.
- Zeng, Q. H., Pei, Z. W., Wang, S. B. and Su, Q. (1999b). Luminescent properties of divalent samarium-doped strontium hexaborate. *Chemistry of Materials*. 11 (3), 605-611.